OXYGEN DIFFUSION AND SELF-DIFFUSION MECHANISMS IN TiNi AND TiAl ALLOYS

Kulkova SE1,2, Bakulin AV1,2

1 National Research Tomsk State University, pr. Lenina 36, 634050 Tomsk, Russia
2 Institute of Strength Physics and Materials Science, Siberian Branch of Russian Academy of Sciences, pr. Akademichesky 2/4, 634055 Tomsk, Russia

ABSTRACT

Using ab initio approach the self-diffusion mechanisms in both B2-TiNi and γ-TiAl alloys are investigated. It is shown that in TiNi self-diffusion is dominated by Ni six-jump cycle [001] mechanism but the contribution of the next-nearest-neighbor mechanism becomes important with temperature increase. In TiAl the diffusion within own sublattice is found to be preferential with Ti as faster diffuser. The common trends in the oxygen diffusion in both alloys are discussed.

KEYWORDS: TiNi, TiAl, OXYGEN, DIFFUSION, AB INITIO CALCULATIONS.

INTRODUCTION

The understanding of the Ti-based alloys oxidation at microscopic level is very important for their technology applications. It is well-known that the biocompatibility of TiNi is resulted from the formation of thin passive TiO2 layers on alloy surface. Since both Ti and Al have affinity to oxygen, the formation of mixed oxide layers is a reason of TiAl low oxidation resistance. The increase of Al diffusivity and decrease of O vacancies formation could be useful to enhance the formation of protective Al2O3 layers on TiAl surface. Thus, the control of alloy component diffusivity and surface oxidation is vital problem for both Ti-based alloys. However, these phenomena are far from complete understanding. The goal of this work is the comparative study of self-diffusion mechanisms and oxygen diffusion in both B2-TiNi and γ-TiAl.

RESULTS AND DISCUSSION

It is known that all atomic diffusion mechanisms such as jumps to nearest-neighbor (NN) or next-nearest-neighbor (NNN) sites, four- or six-jump cycles (4JC and 6JC), antistructural bridge (ASB), require existence of vacancy and/or antistructural atoms. Atomic diffusion in TiNi is dominated by Ni atoms because Ni-vacancy formation energy \( E_f \) is substantial lower than that for Ti one. Our calculations by the projector augmented-wave method confirm this fact: the obtained \( E_f \) values of 1.14 eV and 1.75 eV for Ni and Ti vacancies are in good agreement with earlier results [Lu, 2007] but remain higher than the experimental ones [Weber, 2014]. The migration barrier energies \( E_m \) for atom diffusion along different paths were estimated by using the Climbing Image Nudged Elastic Band method. The activation energies, which are sum of \( E_f \) and \( E_m \) energies, are summarized in Figure 1 for considered self-diffusion mechanisms. It is seen that the lowest migration barrier of 0.82 eV (1.272 eV [Lutton, 1991]) corresponds to the 6JC [001] mechanism that agrees well with the experimental value of 0.87 eV [Kołodziej, 1992]. The difference between 6JC [001] bent and flat mechanism is negligible. The migration barrier for 4JC flat mechanism being insignificantly higher (by \( \sim 0.27 \) eV) than that for the 6JC [001] one, remains lower by 0.54 eV than the barrier for NNN diffusion. In contrast to B2-NiAl alloy [Mishin, 1998] the difference in activation volumes \( V_D \) for considered self-diffusion mechanisms is enough small (Figure 1) and the \( V_D \) values do not contradict experiments [Erdélyi, 2000]. We demonstrate that with increase of temperature the contribution of NNN mechanism becomes more pronounced due to following reasons: (i) the difference in the activation energies becomes not so important; (ii) the chance to complete several-jump cycle decreases because the probabilities of “right” jumps, reverse jumps and the jumps destroying the cycle become almost equal. Finally, we show that the Ni atom jump from the TiNi/TiO2 interfacial layers towards the alloy bulk takes by ~1 eV less energy than reverse jump within NNN mechanism.

In case of \( \gamma \)-TiAl alloy with tetragonal structure \( L1_0 \), diffusion of both components takes place by jumps into the nearest-neighbor sites along own sublattices. This mechanism is known as sublattice self-diffusion (SSD). Contrary to TiNi the effective formation energy of Ti-vacancy (1.73 eV, experiment – 1.38 eV [Kroll, 1992]) is lower than that of Al (2.12 eV). At the same time the migration barrier for Al atom is lower by ~0.1 eV than that for Ti one within SSD mechanism. So, the activation energies for diffusion of Ti and Al atoms are 2.76 eV and 3.06 eV, respectively. The former value is quite close to experimental one (2.59-3.03 eV [Kroll, 1992], [Herzig, 1998]) but the difference in the activation energies for both atoms is substantial lower in comparison with experiment.

![Figure 1: The activation energies and volumes for some self-diffusion mechanisms in TiNi.](image-url)
We investigated the mechanisms of the self-diffusion and the O diffusion in both TiNi and TiAl alloys. It was found that the migration barrier of 0.82 eV for the 6JC [001] bent mechanism of Ni vacancy diffusion is the lowest one among considered mechanisms in TiNi. We demonstrate that with temperature increasing the contribution of NNN mechanism becomes more pronounced. Contrary to TiNi in case of \(\gamma\)-TiAl alloy the jumps of both metal atoms into the nearest-neighbor sites along own sublattices are preferred and Ti is faster diffuser. It was found that the O atom prefers to be absorbed in the Ti-rich octahedral sites in both Ti-based alloys. Since the sorption of oxygen in Ni-rich sites in TiNi takes more energy it prefers to avoid them. In general, the key barriers for O diffusion along preferential paths are comparable.

### CONCLUSION

The work was partly supported by RFBR N 18-03-00064, ISPMS SB RAS (project III.23.1.2), TSU Competitiveness Improvement Program. The calculations were performed on the supercomputers at TSU and MSU.

### ACKNOWLEDGEMENTS

The work was partly supported by RFBR N 18-03-00064, ISPMS SB RAS (project III.23.1.2), TSU Competitiveness Improvement Program. The calculations were performed on the supercomputers at TSU and MSU.

### REFERENCES


